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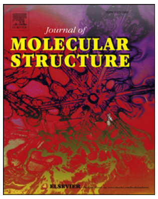

# Hydrogen-bonding interactions between a nitrile-based functional ionic liquid and DMSO

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## ABSTRACT

Task-specific ionic liquids (TSILs) have been introduced by incorporating additional functional groups in the cation or anion to impart specific properties or reactivates. In this work, the hydrogen-bonding interactions between a nitrile-functional TSIL 1-propylnitrile-3-methylimidazolium tetrafluoroborate ([PCNMIM][$BF_4$]) and dimethyl sulphoxide (DMSO) were investigated in detail by attenuated total reflection infrared spectroscopy (ATR-IR), combined with hydrogen nuclear magnetic resonance ($^1H$ NMR) and density functional theory calculations (DFT). It was found that, first, introducing a nitrile group into the alkyl chain does not change the main interaction site in the cation. It is still the C2 hydrogen. So the $\nu$(C2–H) is more sensitive to the environmental change and can be used as an indicator of the environments change of IL. Second, the wavenumber shift changes of $\nu$(C2–H) have two turning points ($x_{DMSO} \approx 0.6$ and 0.9), dividing the dilution process into three stages. Combined with the calculation results, the dilution process is identified as: From larger ion clusters to smaller ion clusters ($x_{DMSO} < 0.6$), then to ion pairs ($0.6 < x_{DMSO} < 0.9$), and finally to individual ions ($x_{DMSO} > 0.9$). Introducing a nitrile group into the alkyl chain does not influence the dilution process of IL dissolving in DMSO. Third, the C≡N in [PCNMIM][$BF_4$] can work as an electron donor in forming hydrogen-bonds with the methyl group of $[PCNMIM]^+$ and DMSO, but its strength is weaker than that formed by the imidazolium ring C–Hs. The dual roles of the cation to work as both electron acceptor and donor expand the wide applications of this nitrile-functional ionic liquid.

## 1. Introduction

Ionic liquids (ILs) are fascinating compounds with unique properties and have received growing interest. In general, they are organic salts with low melting points, normally lower than room temperature [1–4]. Various ILs have been synthesized and their physicochemical properties have been investigated. Unlike ordinary molecular liquids, the ionic nature of ILs results in a combination of unique properties including ultra-low vapor pressure, high thermal and chemical stability, non-flammability, and high solvent capacity [1–4]. These exclusive properties make them useful in many important areas and might potentially be “green” alternatives to conventional organic solvents. Recently, a series of new ILs called task-specific ionic liquids (TSILs) or functionalized ILs have been introduced by incorporating additional functional groups in the cation or anion to impart specific properties or reactivates [5]. TSILs can be considered as a unique subclass of ILs which possess some unique features due to the presence of functional groups which otherwise are not present in the ordinary ILs. The incorporation of a functional group (such as amine, carboxylic and sulfonic acid, ether, nitrile, or alcohol) enriches the choice of ILs for interaction with dissolved substrates in specific ways, resulting in a wider range of applications.

The nitrile group represents a potential electron donor to metals [6]. It can be chemically bonded either to cations or to anions via an alkyl spacer. Nitrile-functionalized ILs were first introduced by Dyson and co-workers [7]. They exhibit high extraction efficiencies of metal ions from aqueous solutions, and have been used as solvents for cobalt-catalyzed cyclotrimerisation reactions of mono-substituted aromatic alkynes, where the nitrile group stabilizes the transient cobalt(I) catalytic species and ensures good conversions [8]. Although the TSILs can be used in wide fields, sometimes their

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high polarity [9], high viscosity [10], and high cost [11] would hinder their large-scale use. Like ordinary ILs, using mixtures of TSILs and polar molecular solvents instead of pure TSILs could be an effective approach to solving these problems.

Hydrogen-bonding interactions play very important roles in governing the physical properties of pure IL and the IL-cosolvent mixtures. A lot of publications can be seen in literature to investigate the hydrogen-bonding interactions in pure ILs and IL-cosolvent mixtures [12–34]. Seddon's group was the first to report the existence of hydrogen-bonds in imidazolium-based ILs [12]. Ludwig's group have performed a lot of studies on hydrogen-bonds in ILs, and they found that strong and directional hydrogen-bonds are formed between cations and anions and can fluidize ionic liquids by destroying the ordered structure [13]. They also found that water in ILs could be a reliable probe to measure the dielectric constant and polarity of ILs [14]. Introducing a nitrile group to ILs may exert significant influence to the properties of the ILs. A lot of studies have been focused on the different properties between the nitrile-functionalized ILs and the ordinary ILs. Most of the researches care about the exo-toxicity of the nitrile functionalized ILs [35]. Little work has been put on the hydrogen-bonding interactions between the co-solvents and ILs before and after introducing nitrile group. DMSO is a widely used solvent, completely miscible with water and very wide range of organic and inorganic substances [36]. It has shown that adding DMSO into ILs can accelerate the cellulose dissolution dramatically [37]. The hydrogen-bonding interactions between DMSO and a few ordinary ILs such as 1-butylpyridinium tetrafluoroborate ([BPy][BF$_4$]) [27] and 1-butyl-3-methylimidazolium tetraborate ([BMIM][BF$_4$]) [34] have been investigated. The interactions between DMSO and nitrile functionalized ILs, however, have not been examined yet, to the best of our knowledge.

In this work, we employ ATR-FTIR, $^1$H NMR, and DFT calculation to study the hydrogen-bonding interactions between 1-propylnitrile-3-methylimidazolium tetrafluoroborate ([PCNMIM][BF$_4$]) and DMSO. Excess infrared spectroscopy [38–42] and two-dimensional correlation spectroscopy (2D-COS) [43,44] have been employed to analyze the infrared spectra. The results are compared with [BMIM][BF$_4$]–DMSO system.

## 2. Experimental section

### 2.1. Materials and sample preparation

[PCNMIM][BF$_4$] (>99%, the water content is less than 0.3%) was purchased from Cheng Jie Chemical (Shanghai, China). DMSO–$d_6$ (>99.8 of deuterium) was from Cambridge Isotopes Laboratories (CIL). DMSO (>99.5%) was purchased from Beijing Chemical Plant (Beijing, China). The ILs were dried for 72 h under vacuum, and then were stored in a desiccator. A series of [PCNMIM][BF$_4$]–DMSO–$d_6$/DMSO binary mixtures were prepared by weighing. The mole fractions of DMSO and DMSO–$d_6$ in the mixtures are approximately 0.99, 0.98, 0.97, 0.96, 0.95, 0.94, 0.93, 0.92, 0.91, 0.90, 0.80, 0.70, 0.60, 0.50, 0.40, 0.30, 0.20, 0.10.

### 2.2. FTIR spectroscopy

FTIR spectra over the range from 4000 to 650 cm$^{-1}$ were collected at room temperature (~25 °C) using a Nicolet 5700 FTIR spectrometer, equipped with an MCT detector. An attenuated total reflection (ATR) cell, made of trapezoidal ZnSe crystal with incident angle of 45° and 12 reflections, was employed in the work. Spectra were recorded with a resolution of 2 cm$^{-1}$, 32 parallel scans, and a zero filling factor of 2. For each sample, three parallel measurements were carried out. The refractive indexes of different solutions were measured with an Abbe refractometer at 25 °C. The formula suggested by Hansen was used to do the ATR corrections [45].

### 2.3. Excess infrared spectroscopy

The theory of excess infrared spectroscopy has been described in detail elsewhere [38,39]. Briefly, an excess infrared spectrum is defined as the difference between the spectrum of a real liquid mixture and that of the respective ideal solution under identical conditions. The working equation in calculating the excess infrared spectrum is

$$\varepsilon^{E} = \frac{A}{d(C_1 + C_2)} - \left(x_1\varepsilon_1^* + x_2\varepsilon_2^*\right) \qquad (1)$$

where $A$ is the absorbance of the mixture, $d$ the light path length, $C_1$ and $C_2$ the molarities of the two components, $x_1$ and $x_2$ the mole fractions of components 1 and 2, $\varepsilon_1^*$ and $\varepsilon_2^*$ the molar absorption coefficients of the two components in their pure states, respectively.

Matlab 7.0 (Math Works Inc., Natick, MA) was used to manipulate spectral data pretreatment, i.e., the subtraction, truncation, and baseline correction, to calculate excess infrared spectra.

### 2.4. Two-dimensional correlation spectroscopy

Standard 2D correlation spectral analysis was performed using Matlab 7.0, based on the algorithm developed by Noda [43]. In order to remove the linear contribution to absorbance by concentration variation and thus to obtain the information of specific interactions, the selected bands were normalized with the modified component-normalization method, namely the bands in the regions of $\nu$(C–Hs) and $\nu$(C≡N) in excess infrared spectra were divided by the corresponding molarity of [PCNMIM][BF$_4$] [41,46]. The average of all the spectra over the full concentration range was used as the reference spectrum. In the 2D correlation contour map, solid (red) and dashed (blue) lines represent positive and negative correlation intensities, respectively.

### 2.5. $^1$H NMR measurements

The $^1$H NMR measurements were carried out on a JEOL JNM-ECA 300 NMR spectrometer (300 MHz) at 298 K. To avoid the influence of the possible interactions between the standard chemical TMS and the samples, TMS was dissolved in CCl$_4$ and used as external standard.

### 2.6. Quantum chemical calculations

All computations were performed with the Gaussian 03 program [47]. The B3LYP method with the 6–31++G** basis set was used to optimize molecular energies, geometries, vibrational frequencies of the isolated DMSO, cation [PCNMIM]$^+$ (denoted as C), anion [BF$_4$]$^-$ (denoted as A), and the following complexes C–DMSO, A–DMSO,CA–DMSO, CCAA, CCAA–DMSO, CCA–DMSO, CCA, CAA, and CAA–DMSO. The optimized geometries at local energy minimum were ensured by the absence of imaginary vibrational frequency.

## 3. Results and discussions

### 3.1. Quantum chemical calculations

Quantum chemical calculations can directly indicate the formation of hydrogen-bonds, so the quantum chemical calculation